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Effect of high pressure on the electrical conductivity of ion conducting polymers

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Abstract--Complex impedance and differential scanning calorimetry (DSC) studies have been carried out on poly(propylene glycol) (PPG) with an average molecular weight of 1025 and poly(ethylene glycol mono-methyl-ether) (PEG) with an average molecular weight of 350, both containing NaCF₃SO₃ in an approximately 20:1 ratio of polymer to salt. The impedance studies were carried out over a range of frequencies, temperatures and pressures. As expected, PEG:NaCF₃SO₃ exhibits the tendency to crystallize while PPG:NaCF₃SO₃ is a glass-forming liquid. The fit to the zero pressure data for PPG:NaCF₃SO₃ using a recently developed generalized Vogel equation (based on a defect diffusion model) is better than that for the standard VTF equation while for PEG:NaCF₃SO₃ the two expressions give about the same level of fit to the data. In the theory, the effect of pressure is due to a pressure dependent critical temperature, T_c , and a defect-defect separation that follows the dimensions of the material. It is found empirically that the pressure dependence of T_c is similar to the pressure dependence of T_g for structurally related polymers containing no salt. However, the details of the relationship between T_c and T_g remain to be determined.

Keywords: Electrical Conductivity, Complex Impedance, Sodium Electrolytes, High Pressure

Chemical Compounds: poly(propylene glycol), poly(ethylene glycol) mono-methyl-ether, NaCF₃SO₃

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INTRODUCTION

Two polymer electrolytes which have received a great deal of attention are poly(propylene glycol) (PPG) and poly(ethylene glycol). There have been a great many experimental studies of various properties of these materials. In the past, two of the authors have reported the results of differential scanning calorimetry (DSC) and high pressure complex impedance studies on the solid (or rubbery) forms of these materials [1-2]. More recently, results have been reported for PPG:Li CF₃SO₃ [3]. The purpose of the present paper is to extend the more recent work to a larger cation (sodium vs. lithium) and to carry out high pressure measurements at temperatures nearer the glass transition temperature, T_g . The results make it possible to further evaluate a recently developed theory of glass-forming materials [4].

EXPERIMENT AND RESULTS

PPG (hydroxyl groups at both ends of each chain) of average MW 1025 and poly(ethylene glycol mono-methyl ether) (hydroxyl group at one end and a methyl ether group at the other end of each chain) of average molecular weight 350 (PEGMME 350 will be referred to in this paper simply as PEG.) were obtained from Polysciences Inc. NaCF₃SO₃ was obtained from Johnson Matthey Catalog Company and was added to the polymers to form a 1M solution (1 mole Na⁺ per liter of solution) which gives an approximately 20:1 repeat unit:sodium ion ratio, using techniques described elsewhere [2]. The equipment and techniques used to measure the electrical conductivity and its variation with pressure and temperature are also described there, together with the details of the DSC measurements.

In all cases, the electrical experiments gave a complex impedance diagram consisting of a slightly depressed semicircular arc and/or slanted line. Those features are usually observed in

ion conducting polymers with blocking electrodes and an example for a closely related material, PPG:LiCF₃SO₃, is shown in Fig. 1 of Ref. 2. The bulk resistance, R, was obtained from the intercept of the arc and/or slanted line with the Z' axis. All of the data for PPG:NaCF₃SO₃ exhibited a sufficient arc so that a Cole-Cole equation could be fit to it [2]. The resistance was transformed to the electrical conductivity, σ , at all temperatures using procedures described elsewhere [2]. It was found that the atmospheric pressure, room temperature conductivities of the as-received PPG and PEG were about 1.2×10^{-10} and 2.2×10^{-7} S/cm, respectively, while those for PPG:NaCF₃SO₃ and PEG:NaCF₃SO₃ were about 1.07×10^{-5} and 4.4×10^{-4} S/cm, respectively. The results for the variation of the zero pressure (vacuum) conductivity with temperature for PPG:NaCF₃SO₃ and PEG:NaCF₃SO₃ are shown in Fig. 1. The DSC data for these materials are shown in Fig. 2.

DISCUSSION

Formalism

All electrical conductivity data were analyzed using a generalized Vogel equation [4]:

$$\sigma(T, P) = \frac{A_\sigma}{T\delta} \exp\left(-\frac{BT_c^{3/2}}{(T-T_c)^{3/2}\delta}\right) \quad (1)$$

where

$$\delta = 1 - \chi(T)P + f(T)P^2 + g(T)P^3 \quad (2)$$

and

$$T_c = T_{co} + \left(\frac{\partial T_c}{\partial P}\right)P + \frac{1}{2}\left(\frac{\partial^2 T_c}{\partial P^2}\right)P^2 \quad (3)$$

A_σ and B are constants. $\delta = V(T, P)/V_o(T)$ where $V(T, P)$ is the volume of the sample and $V_o(T)$ is the volume of the sample at zero pressure. Unfortunately, no PVT data appear to exist for the polymer electrolytes. As an approximation, PVT data for the host polymers were used and the values of δ were obtained by best-fitting eq. (2) to the data given by Zoller and Walsh [5]. T_c is a critical temperature which is assumed to be pressure dependent according to eq. (3). The form of eq. (3) is a result of the fact that T_g is known to be pressure dependent, exhibiting strong curvature, and it is likely that T_g and T_c are related.

Temperature dependence

Fig. 1 shows that the electrical conductivity for PEG:NaCF₃SO₃ exhibits smooth, non-Arrhenius behavior at high temperatures but that there is a large decrease in the conductivity for temperatures below about 265K. This discontinuity is attributed to crystallization, and it is correlated with the DSC results in Fig. 2. The DSC data exhibit a glass transition, with a midpoint glass transition temperature, T_g , of about 204K, as well as a crystallization exotherm at about 228K, followed by a melting endotherm at about 268K.

Fig. 1 also shows that the electrical conductivity of PPG:NaCF₃SO₃ varies smoothly over the entire range of temperatures. This is also consistent with the DSC results shown in fig. 2, where a glass transition is observed for PPG:NaCF₃SO₃ with a midpoint T_g of about 219K, but no signs of crystallization or melting are observed. (PPG containing no salt exhibits a midpoint T_g at about 206K.)

Eq. (1) was best-fit to the zero pressure data shown in Fig. 1. For those data, of course, $\delta = 1$ and $T_c = T_{co}$. The values of the best-fit parameters along with the rms deviations are given in Table I. For comparison, the standard Vogel-Tammann-Fulcher (VTF) [6] equation:

$$\sigma(T, P,) = \sigma_o \exp\left(-\frac{B}{(T - T_o)}\right) \quad (4)$$

was also best-fit to the data. The resultant best-fit VTF parameters for PPG:NaCF₃SO₃ are $\log_{10}\sigma_o=0.324$, $B=1587K$ and $T_o=166.3K$ and those for PEG:NaCF₃SO₃ are $\log_{10}\sigma_o=-0.222$, $B=825K$ and $T_o=182.5K$ and the rms deviations are listed in Table I. The rms deviation for the generalized Vogel equation is lower than that for the VTF equation for PPG:NaCF₃SO₃. On the other hand, the goodness of fit (as measured by the rms deviation) is about the same for the two formalisms in the case of PEG:NaCF₃SO₃. This is not surprising since the temperature range over which the data were taken is closer to T_g in the case of PPG:NaCF₃SO₃ and this is the region that the theory is meant to describe. This result is consistent with previous findings [2,7,8] where fits to the data using an equation similar to eq. (1) known as the BENSH equation [7,9-11] are

better for glass-forming liquids, particularly near T_g . (Eq. (1) and the BENSCH equation differ by the constant in the exponent and the temperature dependence of the pre-exponent.)

Pressure dependence

In all cases, the pressure variation of the electrical conductance, G , is similar to Fig. 3 of Ref. 2 and is reasonably well-represented by:

$$\ln G = \ln G_0 + aP + bP^2 \quad (5)$$

The best-fit values of a and b are listed in Table II.

The coefficients in eq. (5) were transformed to the pressure variation of the electrical conductivity at $P=0$ via:

$$\left(\frac{\partial \ln \sigma}{\partial P} \right)_T = a + \frac{\chi(T)}{3} \quad (6)$$

and

$$\left(\frac{\partial^2 \ln \sigma}{\partial P^2} \right)_T = 2b - 2f(T) + \chi(T)^2 \quad (7)$$

The results are listed in Table II.

First Pressure Derivative

In most previous work, the pressure variation of the electrical conductivity has been analyzed in terms of an activation volume [1-3,12,13]. However, as has been pointed out several times [2,4,12], that formalism does not apply to processes for which a Gibbs energy cannot be identified, and that is the case for most glass-forming liquids, where the non-Arrhenius behavior is observed. Nonetheless, for lack of an applicable theory, the concept of the activation volume has been used anyway. However, the generalized Vogel equation allows a direct calculation of the pressure dependence of the ionic conductivity. It can be shown that eq. (1) leads to the following theoretical expression for the first pressure derivative of the ionic conductivity [4]:

$$\left(\frac{\partial \ln \sigma}{\partial P} \right)_T = \chi - \frac{\chi B T_{co}^{1.5}}{(T - T_{co})^{1.5}} - \frac{1.5 B T T_{co}^{0.5}}{(T - T_{co})^{2.5}} \left(\frac{\partial T_c}{\partial P} \right) \quad (8)$$

Following the procedure given in ref. 4, eq. (8) was best fit to the data using (dT_c/dP) as an adjustable parameter. The best-fit values of (dT_c/dP) are listed in Table I. The theoretical best fit curves are shown in fig. 3 together with the experimental values.

The agreement between the theory and the experiment is quite good except at the highest temperatures for PPG:NaCF₃SO₃. Similar behavior has been observed for the same polymers containing LiCF₃SO₃ [3]. One possible explanation for the difference at high temperature is that the theory is only expected to describe behavior near T_g . However, it is also clear from Eq. (8) that the compressibility dependent terms become more important at high temperatures, and the values of the compressibility are only approximate as they are for the host polymers without salt. Consequently, the reason for the difference between the theory and experiment at high temperature remains to be determined. (The agreement between theory and experiment for PEG:NaCF₃SO₃ is good at high temperature. However, the data do not extend to low temperatures and thus do not represent a test of the ability of the theory to describe data both near and far from T_g .)

It would be interesting to compare the values of (dT_c/dP) with those of (dT_g/dP) since there may be some relation between T_c and the T_g . However, values for (dT_g/dP) do not exist for the ion containing polymers. The only data that appear to exist are for materials that are structurally related to the host polymers [12,14,15] and those values are listed in Table I. It is interesting that the values of (dT_c/dP) are about half the values of (dT_g/dP) and thus both quantities are larger for PPG:NaCF₃SO₃ than for PEG:NaCF₃SO₃. The fact that (dT_c/dP) (and presumably (dT_g/dP)) is larger for PPG:NaCF₃SO₃ than for PEG:NaCF₃SO₃ is partly responsible for the difference in the first pressure derivative of the ionic conductivity between the two materials.

The difference between (dT_g/dP) (related material without ions), and (dT_c/dP) (material with ions) could, of course, be due to the effect of the ions i.e. the ions could change the effect of pressure on T_g in which case (dT_c/dP) could be the same as (dT_g/dP) . That possibility needs to be checked and such experiments are currently underway. On the other hand, it may be that the T_c

is fundamentally different from T_g . Certainly, the value of T_{co} itself, is much lower than the value of T_g so that it will not be surprising if (dT_c/dP) is less than (dT_g/dP) . Interestingly, the value of $1/T_{co}(dT_c/dP)$ for PPG:NaCF₃SO₃ is about 0.61, which is close to the value for PPG:LiCF₃SO₃ (0.62) and for dielectric relaxation in structurally related PPO (high molecular weight (10^6) ParelTM elastomer) containing no ions (0.65) [4]. However, none of these values is close to the experimental value of $1/T_g(dT_g/dP)=0.89$ for pure PPO. Further, the value of $1/T_{co}(dT_c/dP)$ for PEG:NaCF₃SO₃ is about 0.35, which is the same as is observed for PEG:LiCF₃SO₃ [4]. Both of these latter values are smaller than the value of $1/T_g(dT_g/dP)$ of about 0.44 obtained for structurally related PEO (high molecular weight (10^5) poly(ethylene oxide)) containing no ions [14]. Again, the relationship between (dT_c/dP) and (dT_g/dP) remains to be determined.

Second Pressure Derivative

The curvature, as represented by b in Eq. (5), is also of interest. In particular, it has been noted that all of the previously reported values for PPG-based materials [1-3,16,17] are negative. On the other hand, all of the previously reported results for PEG-based materials, to date, are positive [3,18]. In addition, other recent data for a PEG-based electrolyte also show positive curvature [Fig. 2 of Ref. 13].

The results of the present work are slightly different. First, the highest temperature values of b for PPG:NaCF₃SO₃ are positive and the lowest temperature value for PEG:NaCF₃SO₃ is negative. Of more fundamental importance are the values of $(\partial^2 \ln \sigma / \partial P^2)_T$ calculated using eq. (7). As can be seen in Table II, those values are all negative for PPG:NaCF₃SO₃ and become increasingly negative as temperature decreases. The values for PEG:NaCF₃SO₃ are positive at high temperatures and become negative at the lowest temperatures. This behavior is predicted by the generalized Vogel equation. It has been shown that the curvature is given by [4]:

$$\left(\frac{\partial^2 \ln \sigma}{\partial P^2} \right)_T = +\chi^2 - 2f - \frac{1.5BT T_{co}^{0.5}}{(T - T_{co})^{2.5}} \left(\frac{\partial^2 T_c}{\partial P^2} \right) + R \left(\frac{\partial T_c}{\partial P} \right) + Q \left(\frac{\partial T_c}{\partial P} \right)^2 + \frac{2fB T_{co}^{1.5}}{(T - T_{co})^{1.5}} - \frac{2B\chi^2 T_{co}^{1.5}}{(T - T_{co})^{1.5}} \quad (9)$$

where

$$R = -\frac{1.5\chi BT T_{co}^{0.5}}{(T - T_{co})^{2.5}} - \frac{1.5\chi BT_{co}^{0.5}}{(T - T_{co})^{1.5}} - \frac{1.5\chi BT_{co}^{1.5}}{(T - T_{co})^{2.5}} \quad (10)$$

and

$$Q = -\frac{0.75BT T_{co}^{-0.5}}{(T - T_{co})^{2.5}} - \frac{3.75BT T_{co}^{0.5}}{(T - T_{co})^{3.5}} \quad (11)$$

The value of $(\partial^2 T_c / \partial P^2)$ was adjusted to give approximately the correct value for the curvature at the lowest temperature for each set of data and the resultant values of $(\partial^2 T_c / \partial P^2)$ are listed in Table I. The values of $(\partial^2 T_g / \partial P^2)$ for the structurally related host polymers containing no salt are also listed there. As can be seen in Table I, the values of $(\partial^2 T_c / \partial P^2)$ follow the trend for $(\partial^2 T_g / \partial P^2)$, the values of $(\partial^2 T_c / \partial P^2)$ being about one third the values of $(\partial^2 T_g / \partial P^2)$. Thus, both quantities are larger for PPG:NaCF₃SO₃ than for PEG:NaCF₃SO₃. This reinforces the earlier suggestion that there is a relation between T_c and T_g though once again the final determination of its form awaits high pressure experiments on T_g in polymer electrolytes.

The theoretical values for the curvature and the experimental results are plotted in Fig. 4. It is clear that the temperature variation of $(\partial^2 \ln \sigma / \partial P^2)_T$ is reproduced very well by the theory. As was the case for the first derivative, the theory for PPG:NaCF₃SO₃ deviates from the experimental values at the highest temperatures. This is not unexpected as was discussed for the case of the first pressure derivative.

Ionic Conductivity vs. Pressure

As a final test of the generalized Vogel equation, eq. (1) was used to generate the ionic conductivity for PPG:NaCF₃SO₃ over the pressure range of the data at various temperatures. In addition, the ionic conductivity was calculated from the experimental data using:

$$\sigma = \frac{G I_o}{A_o \delta^{1/3}} \quad (12)$$

The results of the theory and the experiment are shown in Fig. 5. It is important to realize that this approach is different from that used above. Earlier in the paper, both the data and the theory were analyzed using a quadratic approximation. This was done primarily because that is the form of most of the data in the literature. However, the theory and experiment shown in fig. 5

represent an exact calculation, though some of the input PVT data are approximate. It is seen that the agreement between the theory and experiment continue to be quite good.

SUMMARY and CONCLUSIONS

In summary, several results have been obtained via DSC and complex impedance studies of PEG and PPG containing sodium salts. The melting process identified in the DSC data for PEG:NaCF₃SO₃ is correlated with a substantial rise in the electrical conductivity of the material. It is confirmed that a generalized Vogel equation gives a better fit to the experimental data for cases where the data are taken over a temperature range that is close to the glass transition temperature. It is also shown that this equation reproduces pressure dependent conductivity data extremely well. In the present application of the theory three adjustable parameters are used for the zero pressure data and two more are used to reproduce the pressure variation. However, the results suggest that there may be a relationship between the fitting parameters T_c , $(\partial T_c / \partial P)$, $(\partial^2 T_c / \partial P^2)$, and the values of T_g , $(\partial T_g / \partial P)$ and $(\partial^2 T_g / \partial P^2)$ which can be measured directly. Consequently, it will probably be possible to reduce the number of parameters empirically. In fact, it has been shown that the dielectric relaxation times in poly(vinyl acetate) can be reproduced by the generalized Vogel equation using only one or two adjustable parameters [4]. More importantly, each of the adjustable parameters has a theoretical basis (and corresponding physical interpretation) and thus, in principle, can be calculated [4]. Work toward predicting the adjustable parameters is currently underway.

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Table I. Quantities relevant to the defect diffusion model.

	PPG: NaCF ₃ SO ₃	PEG: NaCF ₃ SO ₃
Log ₁₀ (D) (D is S-K/cm)	1.72	2.12
B	10.98	8.11
T _c (K)	142.3	140.5
T _g (K)	219	204
Temp Range of Data (K)	228-300	289-351
rms dev (generalized Vogel)	0.004	0.004
rms dev (VTF)	0.007	0.004
$\left(\frac{\partial T_c}{\partial P}\right)_T$ (K/GPa)	86.9	48.5
$\left(\frac{\partial T_g}{\partial P}\right)_T$ (K/GPa)	(196) ^a (142, 172) ^c (192, 184) ^d	(90) ^b
$\left(\frac{\partial^2 T_c}{\partial P^2}\right)_T$ (K/GPa ²)	-135	-42
$\left(\frac{\partial^2 T_g}{\partial P^2}\right)_T$ (K/GPa ²)	(-390) ^a (-207.6, -342) ^c (-433, -355) ^d	(-146) ^b

a. Determined from a graphical analysis of the data for high molecular weight ($\approx 10^6$) PPO (ParelTM elastomer) shown in fig. 4 of ref. 12.

b. Results for high molecular weight ($\approx 10^5$) PEO from ref. 14.

c. Results for PPG 400 from ref. 15.

d. Results for PPG 4000 from ref. 15.

Table II. Effect of pressure on the electrical conductivity for PEG:NaCF₃SO₃ and PPG:NaCF₃SO₃.

T	a	b	$\chi/3^a$	$\left(\frac{\partial \ln \sigma}{\partial P}\right)_T$	$\left(\frac{\partial^2 \ln \sigma}{\partial P^2}\right)_T$
(K)	(GPa) ⁻¹	(GPa) ⁻²	(GPa) ⁻¹	(GPa) ⁻¹	(GPa) ⁻²
PPG:NaCF ₃ SO ₃					
248.1	-45.6	-20.3	0.156	-45.4	-42
257.1	-38.1	-21.2	0.160	-37.9	-44
275.1	-28.85	-8.25	0.171	-28.7	-18
294.8	-22.83	-1.35	0.185	-22.6	-5.0
314.1	-18.0	+0.11	0.202	-17.8	-2.5
334.1	-14.0	+0.36	0.223	-13.8	-2.6
353.3	-11.0	-0.70	0.246	-10.8	-5.3
PEG:NaCF ₃ SO ₃					
296.3	-9.00	-0.34	0.134	-8.87	-1.6
315.1	-7.43	+0.59	0.146	-7.29	-0.03
335.3	-6.82	+1.72	0.161	-6.66	+1.9
355.2	-5.99	+1.74	0.179	-5.81	+1.5
375.2	-5.40	+2.52	0.200	-5.20	+2.6

a. Reference 5.

FIGURE CAPTIONS

Figure 1. Electrical conductivity vs. reciprocal temperature at zero pressure for PEG:NaCF₃SO₃ and PPG:NaCF₃SO₃. The solid lines are the best-fit generalized Vogel equation (eq. 1).

Figure 2. DSC thermograms for PPG:NaCF₃SO₃ and PEG:NaCF₃SO₃. The heating rate is 10 K/min.

Figure 3. $(d \ln \sigma / dp)_T$ vs. temperature for PEG:NaCF₃SO₃ and PPG:NaCF₃SO₃. The concentration is approximately 20:1 repeat units per sodium for each material. The solid lines are the best-fit of eq. (8) (based on the generalized Vogel equation) to the data.

Figure 4. $(\partial^2 \ln \sigma / \partial p^2)_T$ vs. temperature for PPG:NaCF₃SO₃ and PEG:NaCF₃SO₃. The solid and dotted lines are the theoretical values calculated using eq. (9).

Figure 5. Electrical conductivity vs. pressure for PPG:NaCF₃SO₃. The solid lines are the best-fit generalized Vogel equation (eq. 1).

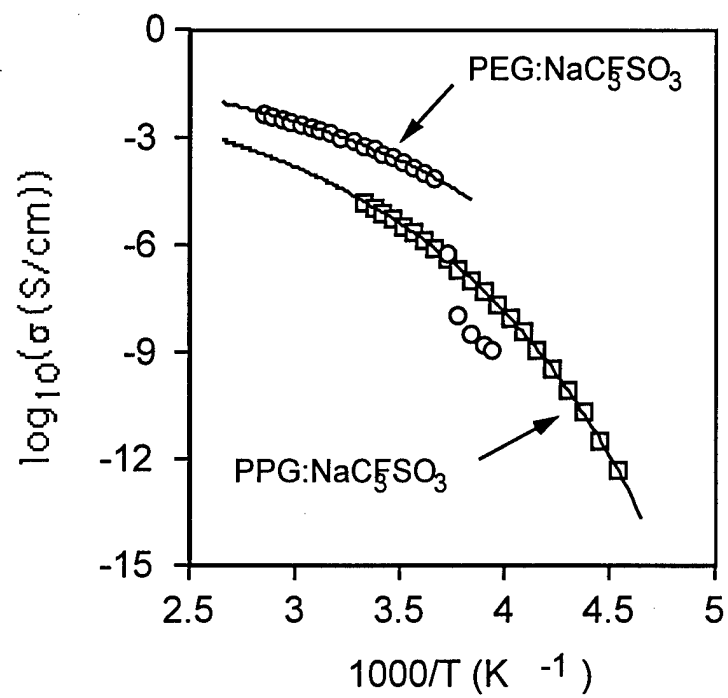


Figure 1
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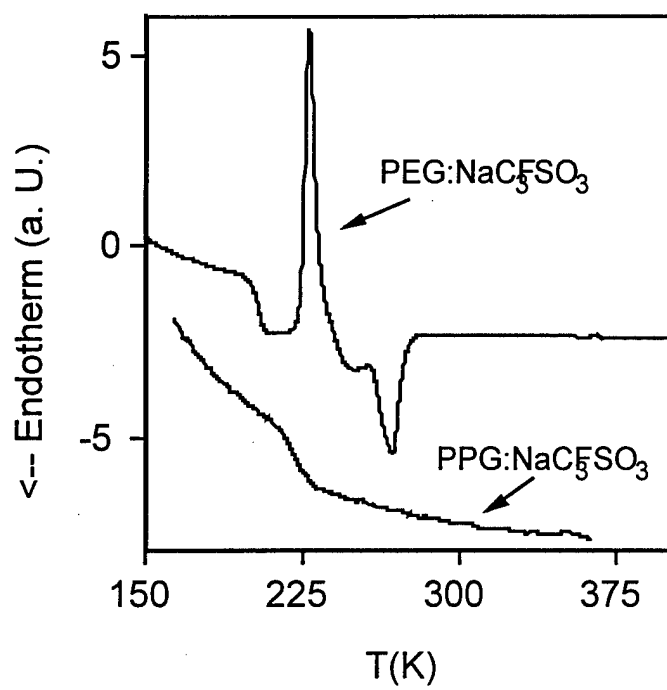


Figure 2
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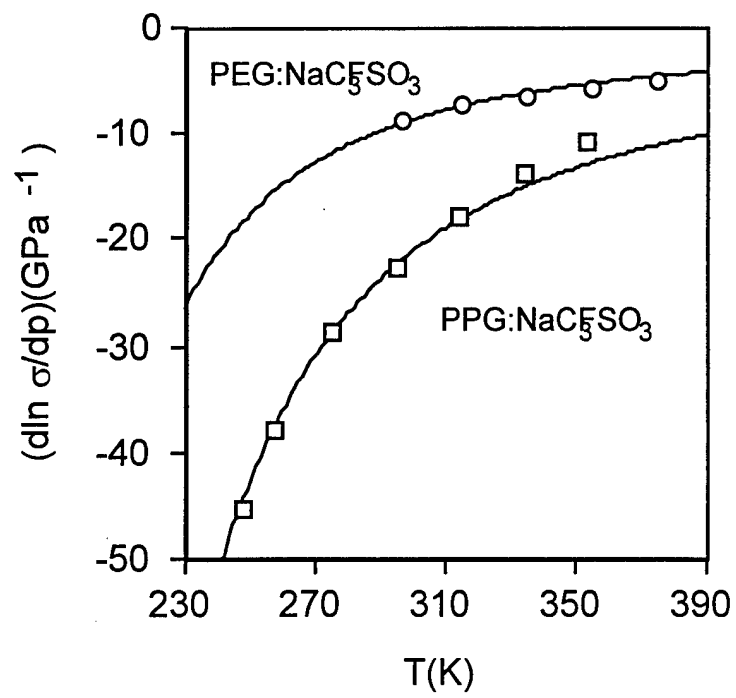


Figure 3

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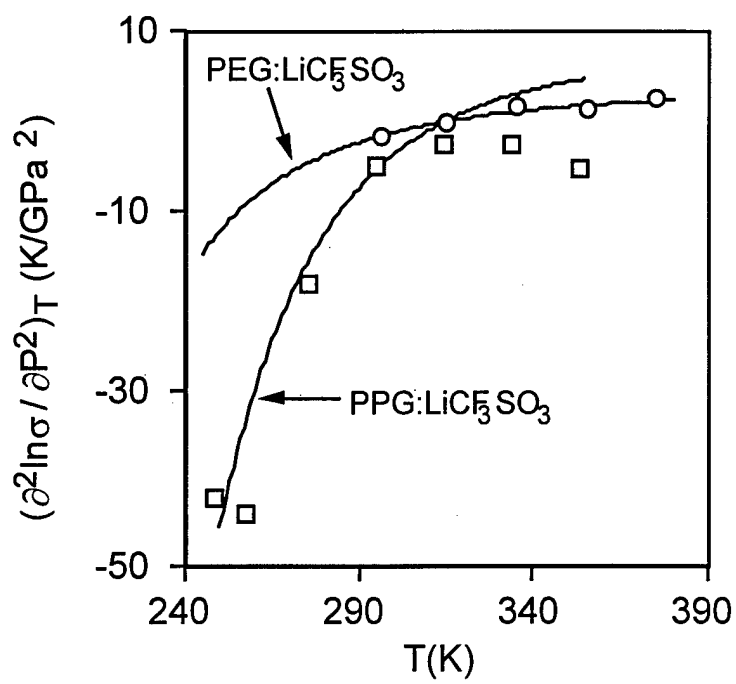


Figure 4

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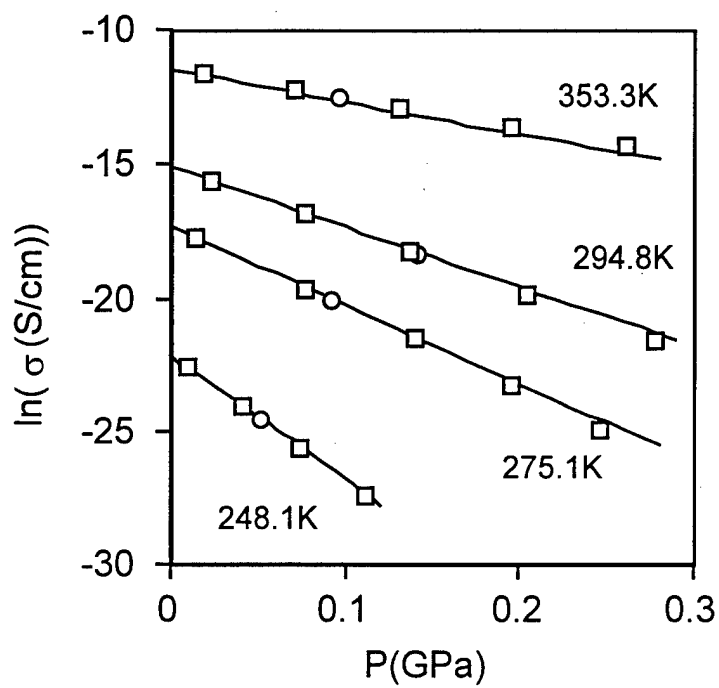


Figure 5

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